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# Silicate cathodes for lithium batteries: alternatives to phosphates?

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Polyoxyanion compounds, particularly the olivine-phosphate  $\text{LiFePO}_4$ , are receiving considerable attention as alternative cathodes for rechargeable lithium batteries. More recently, an entirely new class of polyoxyanion cathodes based on the orthosilicates,  $\text{Li}_2\text{MSiO}_4$  (where  $\text{M} = \text{Mn, Fe, Co}$ ), has been attracting growing interest. In the case of  $\text{Li}_2\text{FeSiO}_4$ , iron and silicon are among the most abundant and lowest cost elements, and hence offer the tantalising prospect of preparing cheap and safe cathodes from rust and sand! This Highlight presents an overview of recent developments and future challenges of silicate cathode materials focusing on their structural polymorphs, electrochemical behaviour and nanomaterials chemistry.

## 1. Introduction

For the next generation of rechargeable lithium batteries, there is intensive research activity targeted on developing new electrode materials, particularly for large-scale use in hybrid electric or pure electric vehicles and in stationary energy storage of solar/wind power [1-3]. Polyoxyanion compounds are receiving considerable interest as alternative cathodes to the conventional intercalation oxides, layered  $\text{LiCoO}_2$  or spinel  $\text{LiMn}_2\text{O}_4$ . The strong binding of the oxygen within polyoxyanions enhances stability and thus safety, compared with transition metal oxides. The electronic inductive effect shifts the d-states of the transition metal ions and hence the redox potentials, providing a means of tuning the latter. Phosphate materials, particularly  $\text{LiFePO}_4$ , have been extensively studied and continue to be important [2,3].

More recently, a new class of polyoxyanion cathodes based on the orthosilicates,  $\text{Li}_2\text{MSiO}_4$  (where  $\text{M} = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}$ ), has been attracting significant attention [4-34]. The relatively strong Si-O bonds promote similar lattice stabilization effects to the phosphate bonds found in  $\text{LiFePO}_4$ . Of these silicates, the most studied is  $\text{Li}_2\text{FeSiO}_4$ , with iron and silicon being among the most abundant and lowest cost elements. Indeed, developing cheap, sustainable and safe cathode materials is a prime target for large scale lithium batteries.

A key feature of the  $\text{Li}_2\text{MSiO}_4$  system is that, in principle, extraction of two lithium ions is possible for a two electron redox process (i.e., operating on both  $\text{M}^{2+}/\text{M}^{3+}$  and  $\text{M}^{3+}/\text{M}^{4+}$  redox couples) especially for the Mn system; this should produce a higher capacity (e.g. above 300 mAh/g for  $\text{Li}_2\text{MnSiO}_4$ ) than the olivine phosphates in which one lithium at most can be extracted.

Although numerous examples are cited, it is beyond the scope of this short review to give an exhaustive summary of all the studies in this highly active field. Rather, this article highlights recent developments of silicate-based cathodes with emphasis on their crystal structures, electrochemical behaviour and nanomaterials chemistry.

## 2. Polymorphism and Defects

$\text{Li}_2\text{MSiO}_4$  compounds ( $\text{M} = \text{Fe, Mn, Co}$ ) belong to a large family of materials known as the tetrahedral structures [35,36]. These structures are composed of tetragonally packed oxide ions (a

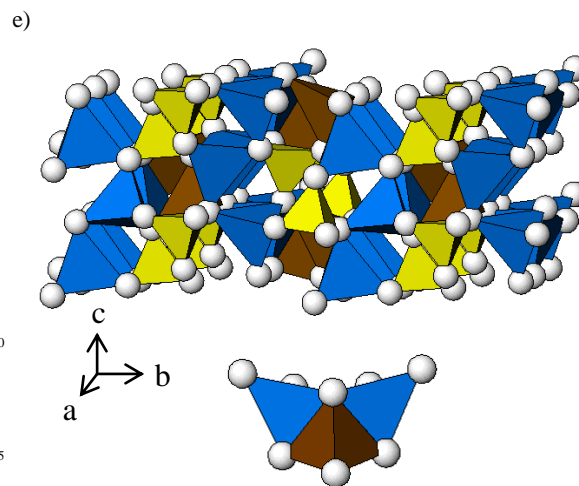
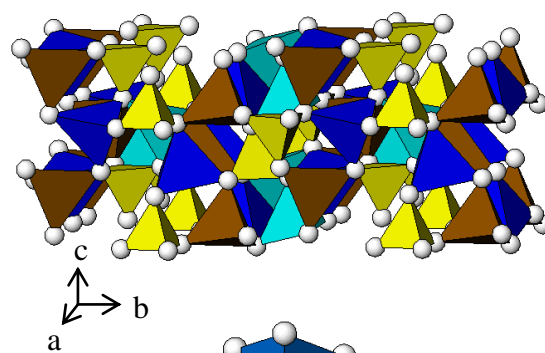
distorted form of hexagonal close packing) within which half the tetrahedral sites are occupied by cations, such that face sharing between the pairs of tetrahedral sites is avoided. The cations can order within the tetrahedral sites in different ways and various structural distortions are possible, leading to a rich and complex polymorphism, as summarised below.

The tetrahedral structures may be divided into two families, designated  $\beta$  and  $\gamma$  (related to the  $\beta$ - and  $\gamma$  polymorphs of  $\text{Li}_3\text{PO}_4$ ). In the  $\beta$  structure all the tetrahedra point in the same direction, perpendicular to the close-packed planes, and share only corners with each other, shown in Figs 1(a), (b). In the case of the  $\gamma$  polymorphs, the tetrahedra are arranged in groups of three with the central tetrahedron pointing in the opposite direction to the outer two, with which it shares edges (Figs 1(c),(d),(e)). Where both  $\beta$  and  $\gamma$  polymorphs exist for a given compound the latter is stable at higher temperatures, with the  $\beta$  to  $\gamma$  transformation involving inversion of half the tetrahedral sites [36]. Several variants of both  $\beta$  and  $\gamma$  exist, involving either ordering or distortions of the parent structures; they are designated  $\beta_1, \beta_{II}, \gamma_0, \gamma_{II}, \gamma_s$  (Fig. 1). In many instances these phases may be quenched to room temperature, where they exhibit long-term stability.

**$\text{Li}_2\text{FeSiO}_4$ .** Several structures have been proposed to describe  $\text{Li}_2\text{FeSiO}_4$ . The first was reported by Nyten et al [5] who suggested an orthorhombic structure (based on  $\beta\text{-Li}_3\text{PO}_4$ ), with space group  $Pmn2_1$  (Fig. 1a). In this structure chains of  $\text{LiO}_4$  tetrahedra run along the  $a$  direction parallel to chains of alternating  $\text{FeO}_4$  and  $\text{SiO}_4$  tetrahedra. Later, Nishimura *et al.* [7] reported the structure of  $\text{Li}_2\text{FeSiO}_4$  prepared at 800°C using a monoclinic space group  $P2_1$ . The structure has been designated by these authors as  $\gamma_s$ , Fig. 1(c). It differs from the other  $\gamma$  structures in that there are no edge sharing trimers of tetrahedra; instead one set of  $\text{LiO}_4$  tetrahedra are arranged in edge sharing pairs with  $\text{FeO}_4$  tetrahedra, whilst the other set of  $\text{LiO}_4$  tetrahedra forms edge sharing pairs with itself, Fig. 1(c). More recently this description has been simplified using the higher symmetry space group  $P2_1/n$  [7b,17].

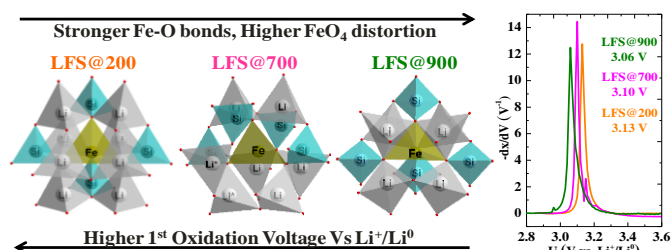
Sirisopanaporn et al [16] have described the crystal structure of a new  $\gamma_{II}$ -polymorph of  $\text{Li}_2\text{FeSiO}_4$ , Fig 1(e), obtained by quenching from 900°C; the structure was established by electron microscopy, XRD, and neutron diffraction; it is

isostructural with  $\text{Li}_2\text{CdSiO}_4$  (space group  $Pmnb$ ), and differs from the  $\gamma_s$  structure obtained by quenching from  $800^\circ\text{C}$  [7]. A simple  $\beta_{\text{II}}$  polymorph (Fig. 1(a)), space group  $Pmn2_1$ , may be prepared by hydrothermal synthesis at low temperature [8].



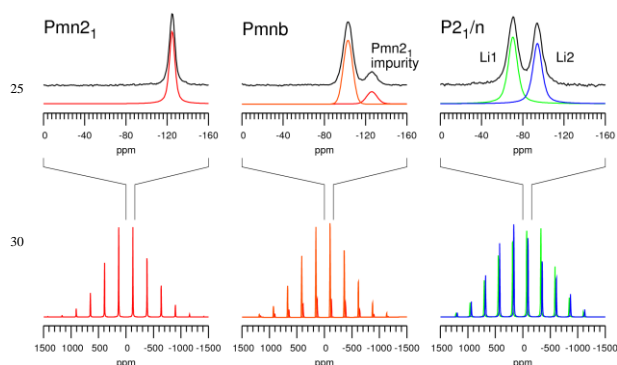
**Fig 1.** Structures of  $\text{Li}_2\text{MSiO}_4$  polymorphs; (a)  $\beta_{\text{II}}$  structure in which all the tetrahedra point in the same direction, perpendicular to the close-packed planes, and share only corners with each other; chains of  $\text{LiO}_4$  along the  $a$ -axis and parallel to chains of alternating  $\text{MO}_4$  and  $\text{SiO}_4$  (b)  $\beta_{\text{I}}$  structure, all tetrahedra point in same direction with chains of alternating  $\text{LiO}_4$  and  $\text{MO}_4$  tetrahedra along  $a$ , parallel to chains of alternating  $\text{LiO}_4$  and  $\text{SiO}_4$  tetrahedra, (c)  $\gamma_s$  structure, half tetrahedra pointing in opposite directions and contain pairs of  $\text{LiO}_4/\text{MO}_4$  and  $\text{LiO}_4/\text{LiO}_4$  edge-sharing tetrahedra (inset), (d)  $\gamma_0$  structure in which the tetrahedra are arranged in groups of three with the central tetrahedron pointing in the opposite direction to the outer two, with which it shares edges; the group of 3 edge-sharing tetrahedra consist of the sequence  $\text{Li-Li-M}$  (inset), (e)  $\gamma_{\text{II}}$  structure in which the group of 3 edge-sharing tetrahedra consist of the sequence  $\text{Li-M-Li}$  (inset).  $\text{SiO}_4$  (yellow);  $\text{MO}_4$  (brown);  $\text{LiO}_4$  (blue); light and dark blue tetrahedra represent crystallographically distinct Li sites.

It has been demonstrated that variations in the  $\text{FeO}_4$  geometry (orientation, size, and distortion) influence the equilibrium potential measured during the first oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  in all polymorphs. Shorter and hence stronger (more covalent)  $\text{Fe-O}$  bonds result in greater splitting in energy between bonding and anti-bonding states, lowering the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox potential vs.  $\text{Li}^+/\text{Li}^0$  (Fig. 2) [18]. Magnetic susceptibility measurements [6] indicate that  $\text{Li}_2\text{FeSiO}_4$  powders prepared at  $800^\circ\text{C}$  possess an antiferromagnetic ordering below  $T_N = 25\text{ K}$  due to long range  $\text{Fe-O-Li-O-Fe}$  interactions.



**Fig 2.** Local environments around  $\text{FeO}_4$  tetrahedra (in green) in the three polymorphs of  $\text{Li}_2\text{FeSiO}_4$ :  $\beta_{\text{II}}$  (LFS@200);  $\gamma_s$  (LFS@700);  $\gamma_{\text{II}}$  (LFS@900). (LiO<sub>4</sub> in grey, SiO<sub>4</sub> in blue) and derivative plots obtained from PITT in the first oxidation of these three polymorphs [18].

**$\text{Li}_2\text{MnSiO}_4$ .** From powder X-ray diffraction (XRD), Dominko et al [8] proposed an orthorhombic  $\beta_{\text{II}}$  structure for  $\text{Li}_2\text{MnSiO}_4$  (based on  $\beta\text{-Li}_3\text{PO}_4$ , space group  $Pmn2_1$ ); they also pointed out the possibility of another  $\gamma_{\text{II}}$ -polymorph ( $Pmnb$ ) detected by electron diffraction. XRD studies by Politaev et al [19] reported a  $\gamma_0$  structure with monoclinic symmetry (space group  $P2_1/n$ ) based on  $\gamma\text{-Li}_3\text{PO}_4$ , similar to that reported for monoclinic  $\text{Li}_2\text{CoSiO}_4$  [32] (Fig. 1d); they also observed a small amount of Li/Mn cation exchange in  $\text{Li}_2\text{MnSiO}_4$ . Atomistic defect modelling studies on  $\text{Li}_2\text{MnSiO}_4$  [20] indicate that the most energetically favourable intrinsic disorder is the Li-Mn anti-site or cation exchange defect, suggesting a small population of Li on Mn sites and Mn on Li sites, dependent on synthesis routes and thermal history.



**Fig 3..**  $^6\text{Li}$  MAS NMR spectra of three  $\text{Li}_2\text{MnSiO}_4$  polymorphs (after ref [15]). The upper part shows isotropic bands and lower part presents the entire manifolds of spinning sidebands.

$^6\text{Li}$  MAS NMR spectroscopy has proved to be a very useful tool to distinguish between different  $\text{Li}_2\text{MnSiO}_4$  polymorphs [15]. Lithium nuclei occupying crystallographically inequivalent lithium sites within a single polymorph exhibited NMR signals at different and well resolved positions (Fig. 3).

Density functional theory (DFT) calculations [9] on orthorhombic  $\text{Li}_2\text{MnSiO}_4$  predict that this phase is unstable on extraction of large amounts of lithium. Arroyo-de Dompablo et al [12] also reported DFT calculations on the thermodynamic stability of  $\text{Li}_2\text{MnSiO}_4$  polymorphs predicting that the lowest energy is found for the  $\beta\text{-Li}_3\text{PO}_4$ -based derivatives. Atomistic defect modelling studies [20] predict favourable  $\text{Al}^{3+}$  dopant

incorporation on the Si site with Li interstitial compensation; this suggests a possible synthesis-doping strategy of introducing additional lithium into  $\text{Li}_2\text{MnSiO}_4$  for higher capacities. Recent DFT-based studies have investigated the electronic structure, structural stability and ion substitution in the  $\text{Li}_2\text{MSiO}_4$  materials [31].

**$\text{Li}_2\text{CoSiO}_4$ .** The third member of the orthosilicate family of cathode materials,  $\text{Li}_2\text{CoSiO}_4$ , has received comparatively less attention [32-34]. Three polymorphic forms ( $\beta_{\text{II}}$ ,  $\beta_{\text{I}}$ , and  $\gamma_0$ ) have been prepared and investigated with powder diffraction and  $^7\text{Li}$  MAS NMR [32,33]. The  $\beta_{\text{II}}$  ( $Pmn2_1$ ) polymorph was obtained by hydrothermal synthesis (150 °C), and subsequent heat treatments yielded the  $\beta_{\text{I}}$  ( $Pbn2_1$ ) form (700°C) and the  $\gamma_0$  ( $P2_1/n$ ) form (1100 °C then quenching from 850°C). Rietveld refinement of X-ray and neutron powder diffraction patterns reveal antisite disorder for  $\beta_{\text{II}}$  with Li on the Co site and Co sharing the Li site (essentially an inverse  $\beta_{\text{II}}$  structure analogous to inverse spinels), very moderate Li/Co mixing for  $\beta_{\text{I}}$ , and no mixing for  $\gamma_0$ .  $^7\text{Li}$  MAS NMR spectra have been recorded for the three forms, and the nature and number of signals were analyzed in relation to the site occupancies for each compound [33].

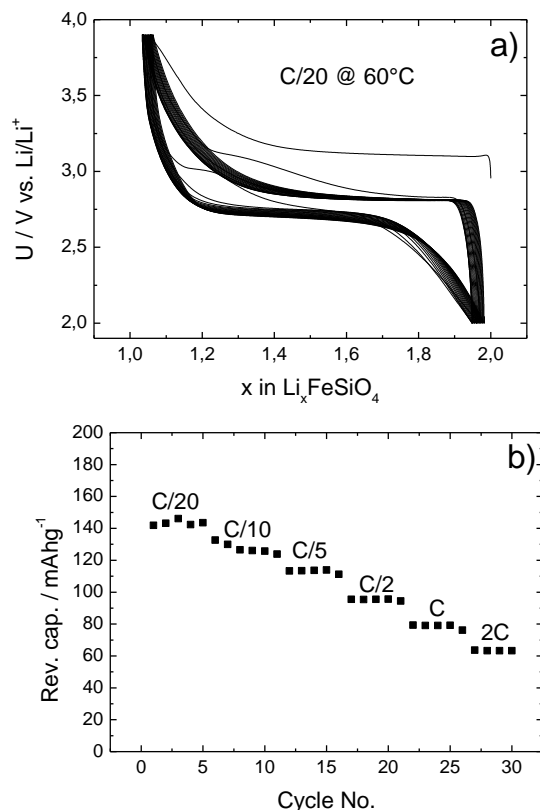
### 3. Electrochemistry and nanomaterials

**$\text{Li}_2\text{FeSiO}_4$ .**  $\text{Li}_2\text{FeSiO}_4$  was shown to undergo an initial charge at voltages above 3V vs Li while subsequent charges were at 2.84V vs Li [5]. Such a shift in potential suggested a change of structure, which was confirmed by X-ray diffraction and Mossbauer spectroscopy during the first two cycles. Studies on the cycled material by neutron diffraction identified conversion from the  $\gamma_s$  structure to a structure corresponding to the inverse  $\beta_{\text{II}}$  (originally observed for  $\text{Li}_2\text{CoSiO}_4$ , described above) [5a,18]. Further studies to investigate such structural changes are warranted, and efforts will doubtless be directed towards the synthesis of polymorphs that are stable from the outset to ensure the electrochemistry does not change on cycling.

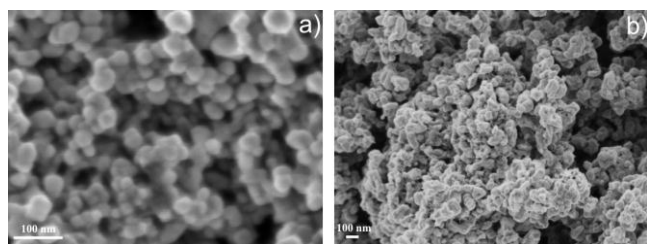
Most of the reported electrochemical studies were conducted at elevated temperatures (e.g 60 °C) to improve the rate performance and increase capacity. Typical capacities are 120-140 mA h g<sup>-1</sup> in the voltage range below 4V vs. Li (Fig 4) [24, 28]. The cycling stability of the  $\text{Li}_2\text{FeSiO}_4$  cathode after conversion to the  $\beta$  phase is good [14]. However, due to low intrinsic conductivity, the rate performance needs to be improved to a similar degree to  $\text{LiFePO}_4$  in order to become competitive for commercial applications. By analogy with  $\text{LiFePO}_4$ , the strategy has been to reduce the particle size and to use carbon coatings (Fig. 5) [4,8,14,22]. In practice, this strategy usually involves the addition of a carbon precursor (citrate anion, ethylene glycol, etc.) that also acts as a complexing agent promoting the formation of a homogeneous gel. The presence of carbon during heat treatment suppresses active particle growth and particle agglomeration [8,10].

Yang and co-workers have made a number of advances in synthetic methods; for example Gong et al [22] reported a carbon-coated  $\text{Li}_2\text{FeSiO}_4$  material with uniform nanoparticles (~40-80nm) from a hydrothermal-assisted sol-gel process; this showed a discharge capacity of 160 mAh g<sup>-1</sup> at C/16 rate, and almost no capacity loss up to 50 cycles. Zhang et al [24] reported

a sol-gel method based on citric acid to prepare  $\text{Li}_2\text{FeSiO}_4$  in which the citric acid acts as both a chelating agent and a carbon source in the synthetic process; they observed a maximum discharge capacity of  $153.6 \text{ mAh g}^{-1}$  in the third cycle, with 98.3% of this capacity retained after 80 charge-discharge cycles.



**Fig 4.** Electrochemical properties of  $\text{Li}_2\text{FeSiO}_4$ ; (a) Discharge-charge curves for samples at C/20 rate. (b) Cycling performance at different current densities (marked as C-rates). [10, 14]



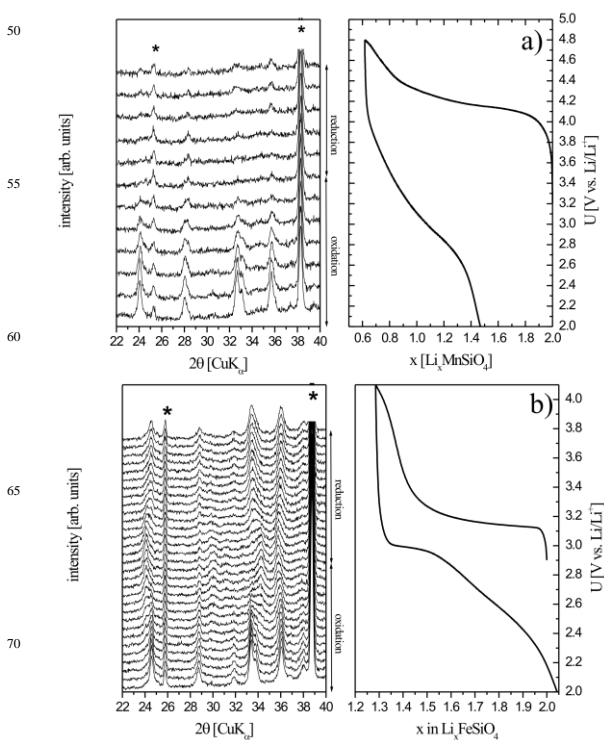
**Fig. 5:** SEM micrographs of  $\text{Li}_2\text{FeSiO}_4$  obtained by a) modified Pechini synthesis method [10] and b) hydrothermal synthesis method [14].

Manthiram and co-workers [28] have synthesized nanostructured  $\text{Li}_2\text{FeSiO}_4$  and  $\text{Li}_2\text{MnSiO}_4$  by a facile microwave-solvothermal process; they report that the  $\text{Li}_2\text{FeSiO}_4/\text{C}$  nanocomposite exhibits good rate capability and stable cycle life, with discharge capacities of  $148 \text{ mAh g}^{-1}$  at room temperature and  $204 \text{ mAh g}^{-1}$  at  $55^\circ\text{C}$ , whereas  $\text{Li}_2\text{MnSiO}_4/\text{C}$  suffers from poor rate capability and drastic capacity fade. Capacities greater than  $200 \text{ mAh g}^{-1}$ , have been observed by several groups. Such capacities exceed the theoretical value for  $\text{Fe}^{2+/3+}$  redox couple

( $166 \text{ mAh g}^{-1}$ ); the results have been interpreted as implying either  $\text{Fe}^{4+}$  formation and/or electrolyte degradation.

Photoelectron spectroscopy (PES) has been used by Thomas and co-workers [5c] to examine the  $\text{Li}_2\text{FeSiO}_4$  cathode surface extracted from lithium-ion batteries; a thin surface film is formed on electrochemical cycling of  $\text{Li}_2\text{FeSiO}_4$  electrodes at  $60^\circ\text{C}$  using a  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  salt based electrolyte, with high salt stability and only small amounts of solvent reaction products. It is suggested that the excellent capacity retention observed (<3% over 120 cycles) during the first cycle is probably a result of this thin surface film [5c].

**$\text{Li}_2\text{MnSiO}_4$ .**  $\text{Li}_2\text{MnSiO}_4$  could be viewed as an attractive cathode material, in terms of energy density and possibility of >1-electron redox process since the higher manganese oxidation state  $\text{Mn}^{4+}$  is more accessible than  $\text{Fe}^{4+}$ .  $\text{Li}_2\text{MnSiO}_4$  is found to have a redox potential near 4.1V vs Li, but initial studies show substantial irreversible capacity loss [8-11]. *in-situ* XRD studies indicate that for  $\text{Li}_2\text{FeSiO}_4$  cycling proceeds through a plateau relating to a two-phase mechanism, whereas lithium exchange from  $\text{Li}_2\text{MnSiO}_4$  involves the formation of an amorphous phase along the oxidation plateau at approximately 4.1V (Fig. 6) [10,23].



**Fig 6.** *in situ* X-ray diffraction patterns and voltage profiles for  $\text{Li}_2\text{MSiO}_4/\text{C}$  at C/50 rate [10] (a)  $\text{Li}_2\text{MnSiO}_4$  (b)  $\text{Li}_2\text{FeSiO}_4$ . Bragg reflections marked with asterisk denotes *in situ* cell reflections.

Li et al [23] have reported the synthesis of a high capacity  $\text{Li}_2\text{MnSiO}_4/\text{C}$  nanocomposite material with good rate performance and a reversible capacity of  $209 \text{ mAh g}^{-1}$  in the first cycle; their XRD and IR results also indicate that the poor cycling behavior might be due to an amorphization of the silicate

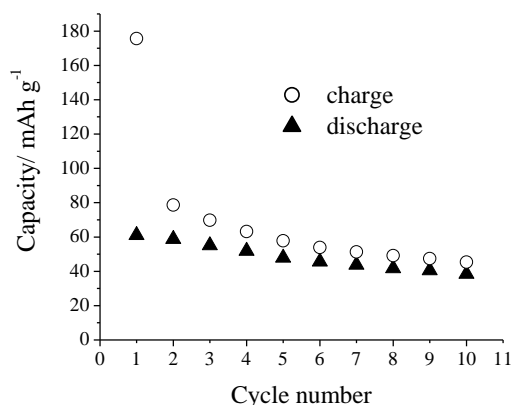
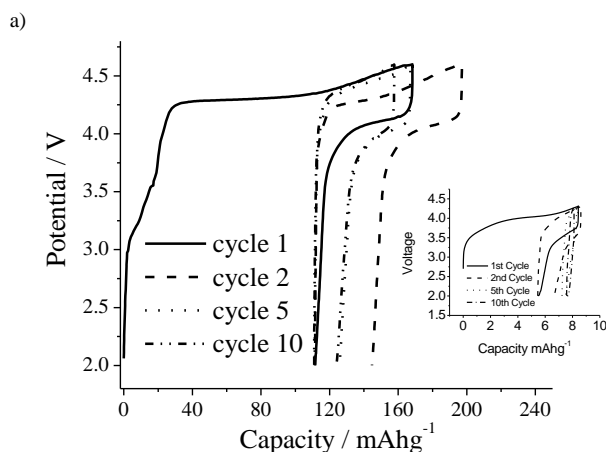
material. Aravindan et al [30] have recently employed an adipic acid assisted sol-gel route to prepare  $\text{Li}_2\text{MnSiO}_4$  nanoparticles, with their  $\text{Li}/\text{Li}_2\text{MnSiO}_4$  cell delivering a stable discharge capacity profile ( $\sim 125 \text{ mAh g}^{-1}$ ) for up to 50 cycles.

Due to problems with the pure Mn-based material, there have been recent studies on mixed-cation  $\text{Li}_2(\text{Fe},\text{Mn})\text{SiO}_4$  solid solutions [13,21]. Preliminary studies on mixed-metal materials suggest the use of the  $\text{Li}_2\text{Fe}_{0.5}\text{Mn}_{0.5}\text{SiO}_4$  composition. The basic concept was to stabilize the local environment of  $\text{Mn}^{3+}$  in tetrahedral coordination by introducing Fe as a “stabilizer”, in line with DFT-based calculations [9]. Gong et al [21] reported an optimal composition of  $\text{Li}_2\text{Fe}_{0.5}\text{Mn}_{0.5}\text{SiO}_4$  that delivers high capacity ( $214 \text{ mAh.g}^{-1}$ ) within a wide voltage window, but with serious capacity fade during cycling.

Studies on  $\text{Li}_2\text{Fe}_{0.8}\text{Mn}_{0.2}\text{SiO}_4$  show good reversibility with a large voltage polarisation in the formation cycles [13]. Using *in-situ* Mössbauer spectroscopy and XANES it was shown that most of the iron was reversibly oxidised to  $\text{Fe}^{\text{III}}$ , while only a part of the manganese was reversibly oxidised to  $\text{Mn}^{\text{III}}$ . Importantly, neither iron nor manganese in the tetravalent state was detected [13]. Future studies are likely to explore whether the performance of other mixed-metal solid solutions proves superior to the pure compounds as found in the case of the layered  $\text{LiMO}_2$  cathodes (e.g.  $\text{Li}(\text{Co}_{1/3}\text{Mn}_{1/3}\text{Ni}_{1/3})\text{O}_2$ ) [2].

**$\text{Li}_2\text{CoSiO}_4$ .** Lyness et al [32] show that the three polymorphs of  $\text{Li}_2\text{CoSiO}_4$  exhibit electrochemical activity when ball-milled, although with severe capacity fading after a few cycles, which is also the case for the corresponding cobalt-based phosphate,  $\text{LiCoPO}_4$ . For the  $\beta_1$  polymorph, coating the prepared material with carbon switches on electrochemistry without the need for ball-milling and gives superior charge capacity ( $170 \text{ mA h g}^{-1} \equiv 1.1 \text{ Li}$  per formula unit) and cyclability, compared with the same phase when ball-milled with carbon (Fig. 7). Only one Li could be extracted up to 4.6 V in agreement with theoretical predictions.

Gong et al [34] have prepared  $\text{Li}_2\text{CoSiO}_4$  by a solution-hydrothermal route, and find reversible lithium extraction/insertion at 4.1V vs Li, but limited to 0.46 lithium per formula unit for the  $\text{Li}_2\text{CoSiO}_4/\text{C}$  composite materials, with a reported charge capacity of  $234 \text{ mAh g}^{-1}$ .



**Fig.7.** Electrochemical properties of  $\text{Li}_2\text{CoSiO}_4$ ; a) Variation of voltage with state of charge (Li content) on cycling the  $\beta_1$  polymorph carbon coated by the xerogel process at a rate of  $10 \text{ mA g}^{-1}$ . Inset shows performance of uncoated material. b) Variation of discharge capacity with cycle number for the carbon-coated  $\beta_1$  polymorph cycled between 2.0 and 4.6 V at  $10 \text{ mA g}^{-1}$  [32].

## 4. Conclusions and future outlook

This review has highlighted an important class of polyoxoanion compounds based on the orthosilicates,  $\text{Li}_2\text{MSiO}_4$  (where  $\text{M} = \text{Mn}, \text{Fe}, \text{Co}$ ), which are attracting growing interest as possible low-cost and safe cathodes for new generations of rechargeable lithium batteries. It serves to illustrate the value of fundamental studies of new materials, including the synthesis and characterisation of silicate polymorphs. However, there are a number of important challenges facing the silicates before they could be considered as viable cathodes and especially as alternatives to  $\text{LiFePO}_4$ . The challenges have been discussed above and are summarised here.

(i) For all  $\text{Li}_2\text{MSiO}_4$  compounds there are significant differences between the first charge and subsequent cycling, which is indicative of structural changes, possibly involving Li/M cation exchange. Further fundamental studies to investigate these structural changes are warranted. In addition to crystallographic studies of the average structure, increasing use of local structure techniques and computer modelling to probe local defects, nano-scale structures, and Li-ion conduction pathways, will be important. Efforts will doubtless be directed to the preparation of polymorphs that are stable from the outset to ensure the electrochemistry does not change on cycling.

(ii) Although the components, Fe, Mn, Si, are low cost, so also must the synthesis methods and their precursors, if truly low cost electrodes are to be obtained. Furthermore the synthesis methods must be scalable.

(iii) The rate capability needs to be improved. This will necessitate a better understanding of the origins of the low rate; especially studies of ionic and electronic transport and the kinetics of phase transitions. Optimising the rate performance will doubtless involve the synthesis of nanostructured materials, the control of particle size and morphology, and the use of chemical doping and surface coatings.

(iv) Higher capacities than are associated with one Li per formula unit ( $170 \text{ mAh g}^{-1}$ ) are desirable, preferably with higher voltages



such as those associated with  $\text{Li}_2\text{MnSiO}_4$ . Modifying the stoichiometric materials to enhance the Li composition range will be important.

(v) Most studies have concentrated on pure  $\text{Li}_2\text{MSiO}_4$  compositions, which are a necessary prelude to studying solid solutions of  $\text{Li}_2\text{MSiO}_4$ , with mixed M of Fe, Mn and Co. It will be interesting to see whether the performance of such mixed-metal solid solutions proves superior to the pure phases as observed in the case of the layered  $\text{LiMO}_2$  cathodes (e.g.  $\text{Li}(\text{Co}_{1/3}\text{Mn}_{1/3}\text{Ni}_{1/3})\text{O}_2$ ), and therefore of technological significance.

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## Notes and references

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